Material Characteristics of Spin-On Glasses for Interlayer Dielectric Applications

Pei-Lin Pai,*,[1] Arun Chetty,[2] Robert Root,[3] Neal Cox, and Chiu Ting**

Intel Corporation, Components Research, Santa Clara, California 95051

ABSTRACT

The material properties of several commercial spin-on glasses were investigated. Infrared spectrophotometry was used to study the annealing effects on the contents of hydroxyl and organic groups. Their concentrations are found to be sensitive to the annealing temperatures and annealing ambients. Both the room-temperature stress and the *in situ* stress during annealing were monitored. The measured stress levels of films on Si wafers are low (less than 10^8 Pa in tensile) compared to other deposited silicon dioxide films. Dielectric properties, including dielectric constants and dissipation factors, were also examined as a function of annealing conditions. A strong correlation between the dielectric properties and the OH content in the film was established. Of the two films studied most extensively, one showed significantly better dielectric properties following low-temperature (<600°C) curing. Both are good dielectric films for VLSI interlayer dielectric applications if high-temperature annealings are allowed.

As device dimensions are scaled into the submicron region and layouts become more complex, multilevel interconnections have become imperative in very large scale integration (VLSI) circuit designs to improve the speed performance and to save chip area. However, the high aspect ratios resulting from multilevel processing impair the step coverage of successive depositions and the resolution of further lithography steps. Therefore, planarizing interlayer films are widely used to smooth out the topography. Among the proposed candidates, etch-back processes (1, 2), bias-sputtered quartz (3, 4), and spin-on dielectric films have been studied quite extensively. Both organic and inorganic spin-on films have been proposed as planarizing layers. Polyimide (5, 6) is an important representative of the organic group. Although polyimide has many advantages, it also poses serious compatibility issues with the standard IC fabrication process due to its significant water absorption, limited thermal stability, and low mechanical rigidity for wire bonding. Spin-on glasses (SOG) as inorganic planarizing films have been under intensive study recently as alternatives to polyimide and other organic spin-on films (7).

Silicate (7-9) and polysiloxane (10-14) are the two most widely used spin-on glass materials. Silicate spin-on films solidify at very low temperatures (≈200°C) and crack easily when the films get thicker (≈4000Å), particularly over surface topography. Its applications are, therefore, limited to very thin layers. Polysiloxane can be deposited as a much thicker film (>5000Å) without cracking. After low- to medium-temperature (<600°C) curing, the polysiloxane films still contain some organic materials, such as methyl, ethyl, or phenyl groups, as well as polymer-bound hydroxyl groups. The amounts vary significantly depending upon the type of SOG and the curing process. After the final annealing at high temperatures (>900°C), most of these organic groups are oxidized, and essentially a silicon dioxide film can be obtained.

In preparation for the study discussed here, we evaluated many commercially available polysiloxane products. These materials were studied for their film-forming properties such as thickness uniformity over the entire wafer, and for their crack resistance when coated over aluminum steps. Two SOG's with the best coating properties were then chosen for this more detailed study. They are designated as SOG-A and SOG-B. Both materials can provide a striation-free film with uniform thickness across the entire wafer, and the film is crack-free over 1 μm aluminum steps. SOG-A contains methyl, phenyl, and ethoxy groups with carbon content in the range of 20-30%. SOG-B has a similar carbon content as SOG-A and contains only methyl and unspecified alkoxy groups bonded to silicon atoms. The solvent for SOG-A is primarily propanol and the solvent for SOG-B is primarily butanol. SOG-B also contains a "leveling agent" to assist in obtaining a uniform coat. Overall, the higher boiling point solvent and the added leveling agent give SOG-B a better coating uniformity than SOG-A.

Experiment Descriptions

All of the SOG samples are prepared using a standard manual photoresist spinner. For each coating, about 3 cm^3 of spin-on glass is dispensed onto a 100 mm Si wafer. This is followed by a 1000 rpm spread cycle for 5s and then a 3000 rpm spin cycle for 20s. Two baking cycles in Blue M convection ovens (100°C for 30 min and 200°C for additional 30 min) are used to drive the casting solvent from the film to complete the SOG film preparation. These SOG films are then annealed under various conditions to study the effects of annealing on the film properties. Unless otherwise specified a standard diffusion furnace is used for these annealings. The annealing temperature ranges from 400° to 950°C, with two ambients: oxygen and nitrogen. For the material studies, the samples are analyzed after the low-temperature spin bake cycles and following the anneal. For the dielectric studies, a sputtered aluminum film is patterned to form the electrodes on top of the SOG films.

The film thickness was measured with a Nanospec AFT and the refractive index measured with a Rudolph ellipsometer. A Fourier transform infrared (FTIR) spectrophotometer was used to measure the IR absorption spectra of the films. Room-temperature stress was measured using an in-house optically levered stress gauge (OLSG) (15-16). Another specially designed hot-stage stress gauge (HSSG) was used to determine the *in situ* stress variation during annealing. The capacitances with the spin-on glass film as the dielectric were measured with an HP 4275A multifrequency LCR meter. The dielectric constant was calculated from the capacitance, the electrode area, and the film thickness.

Results and Discussion

IR spectra.—The FTIR absorption spectra of bare silicon wafers were measured using the Nicolet 60SX FTIR. The digitized spectra were stored on a hard disk. The 0.22 μm SOG films were then spin-coated onto the wafer, subjected to cure at 200°C, and the FTIR spectra measured. Finally the films were cured at 450°, 600°, and 900°C in different ambients and the FTIR spectra taken. Special spectra features due to the substrate were eliminated by subtracting the appropriate bare wafer spectrum from the SOG-coated spectrum. The IR spectra of SOG-A annealed at 450°, 600°, and 920°C in N_2 ambient

*Electrochemical Society Student Member.
**Electrochemical Society Active Member.
[1]Present address: University of California, Berkeley, California 94720.
[2]Present address: Massachusetts Institute of Technology, Cambridge, Massachusetts [illegible]
[3]Present address: Stanford University, Stanford, California 94305.

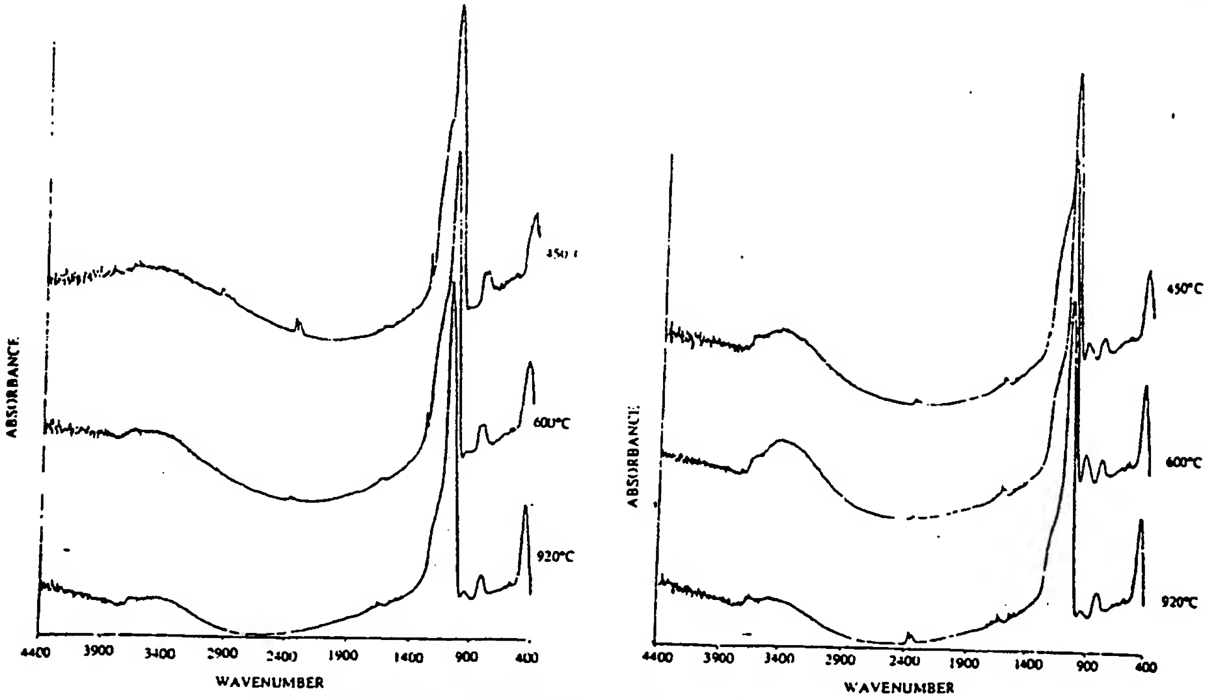

Fig. 1. The IR spectra of SOG-A after annealing in (a, left) N_2 and (b, right) O_2

are shown in Fig. 1a for the range between 400 and 4000 cm^{-1}, while Fig. 1b gives the data for samples annealed in O_2 ambient. All the measurements were made at room temperature in a dry nitrogen ambient. The most intense absorption peak of Si—O bonds, due to the asymmetric stretching mode, is located between 1060 and 1080 cm^{-1}. The location of this peak changes with annealing temperature and ambient as shown in Fig. 2. Both curves shift to lower wave numbers at 450°C and both reverse that shift after annealing at higher temperatures. The initial shift (450°C) is smaller for the sample subjected to the oxygen anneal. The peak for the oxygen-annealed sample shifts to its final position by 600°C, as opposed to the nitrogen-annealed sample, which still has significant shifts between 600° and 920°C. The results shown in Fig. 2 are consistent with the more general observation, to be presented below, that the oxygen ambient causes compositional changes to occur at lower temperatures than does the nitrogen ambient.

There are two absorption peaks associated with OH bonds in the film: the peak at 940 cm^{-1} and the extended region between 3200 and 3800 cm^{-1}. The broader peak between 3200 and 3800 cm^{-1} is the sum of the absorption peaks associated with the OH bonds, with the absorbed water and remaining solvent, while the 940 cm^{-1} peak arises from the stretch of silicon-bound hydroxyl (silanol). The areas under these two peaks which give the relative concentration of these OH content were integrated by the FTIR system and are shown in Fig. 3 as a function of the annealing temperature for SOG-A. The OH profile for the O_2 annealed films in Fig. 3a follows closely to the Si—OH profile under the same annealing conditions shown in Fig. 3b, indicating the amount of absorbed water/solvent is small. However, using the 920°C data as a reference, the film annealed in N_2 shows a larger absorption peak at 450° and 600°C in the 3200-3800 cm^{-1} ranges compared to the Si—OH peak at 940 cm^{-1}. This shows that the film contains some water/solvent molecules even after 450° and 600°C annealing. It is worth noting that the OH concentration is consistently lower when annealed in the N_2 ambient than that in the O_2 ambient and the highest absorption occurs after 600°C annealing in O_2. Annealing at 920°C in either ambient reduces the OH content to a low level.

One of the main residues in the cured film is silicon-bound methyl groups. The stretching mode of Si—CH_3 gives a peak at 1270 cm^{-1} in the IR spectra. The areas under the Si—CH_3 peak of SOG-A films are plotted against the annealing temperature in Fig. 4. In N_2, the organic group concentration decreases less than 5% after the 450°C annealing. Even after 600°C in N_2 for 30 min, more than half the methyl groups remain in the SOG-A film. All the organics are gone after annealing at 920°C. As previously mentioned, O_2 is a more effective ambient in oxidizing organics. Two thirds of the methyl groups are gone after 30 min at 450°C in O_2 and at 600°C or above, almost all of them are gone. The difference between the two annealing ambients in the temperatures required to remove all the organics confirms the observations made from the positional changes of the main Si—O peaks in Fig. 2.

The complex behavior of the Si—O peak position depicted in Fig. 2 must be considered in light of all the complicated compositional changes that occur during curing. This is because the presence of water/solvent, organics, and silicon-bound hydroxyl should each have an impact upon the strength of the Si—O polymer bond. The shift of the Si—O peak to lower wave numbers is attributed to loss of water/solvent due to heating in the 200°-450°C range. However, the oxygen ambient is more

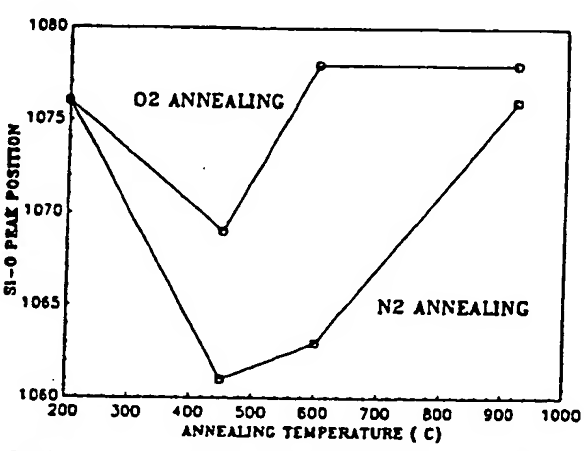

Fig. 2. Si—O peak positions vs. annealing temperatures for SOG-A

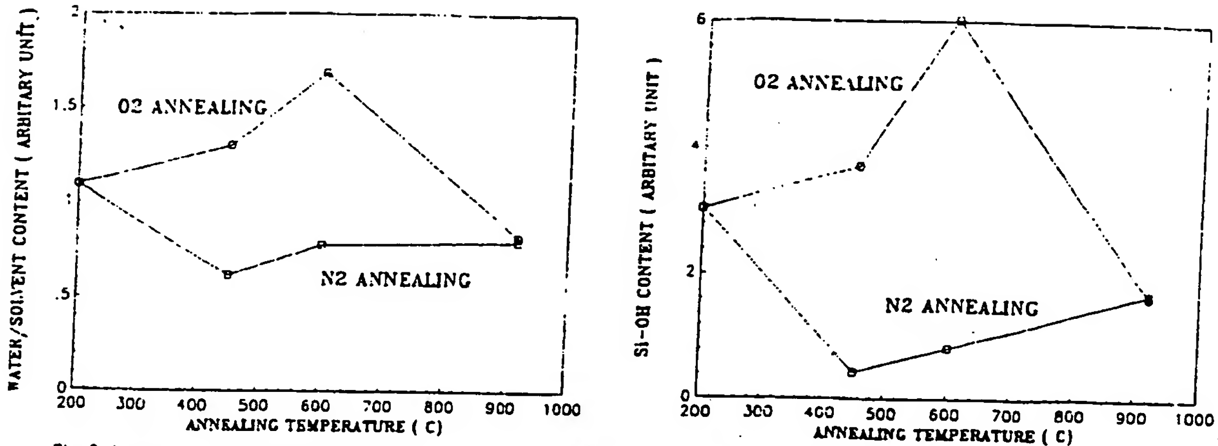

Fig. 3. Integrated IR peak areas for SOG-A vs. annealing temperatures for (a, left) the extended OH peak (3200-3800 cm^{-1}) and (b, right) Si—OH peak (940 cm^{-1}).

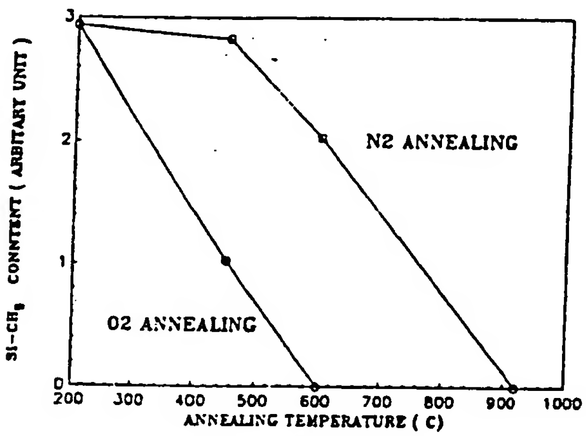

Fig. 4. Integrated Si—CH_3 peak areas for SOG-A vs. annealing temperatures.

effective than nitrogen at low temperatures in removing organics and in adding Si—OH. The loss of organics and the addition of Si—OH is assumed to have the effect of shifting the Si—O peak to higher wave numbers. Thus, while a 450°C anneal in either oxygen or nitrogen causes a shift to lower wave numbers due to water/solvent loss, the shift is less for oxygen ambient since more organics have been lost and significant Si—OH has been formed as a result. In oxygen ambient, the formation of Si—OH appears to be an important step that mediates the loss of organics at low temperatures, and the formation of glassy SiO_2. The glass formation under nitrogen does not occur until above 600°C. In this case, Si—OH formation may not be a significant intermediate step.

The IR spectra of SOG-B are shown in Fig. 5 with the same annealing conditions as in Fig. 1. The locations of the main Si—O peak for different annealing temperatures and ambients are shown in Fig. 6. The compositional changes invoked to explain the peak shifts of SOG-A can be used to explain the behavior shown in Fig. 6 for SOG-B. It illustrates some significant differ-

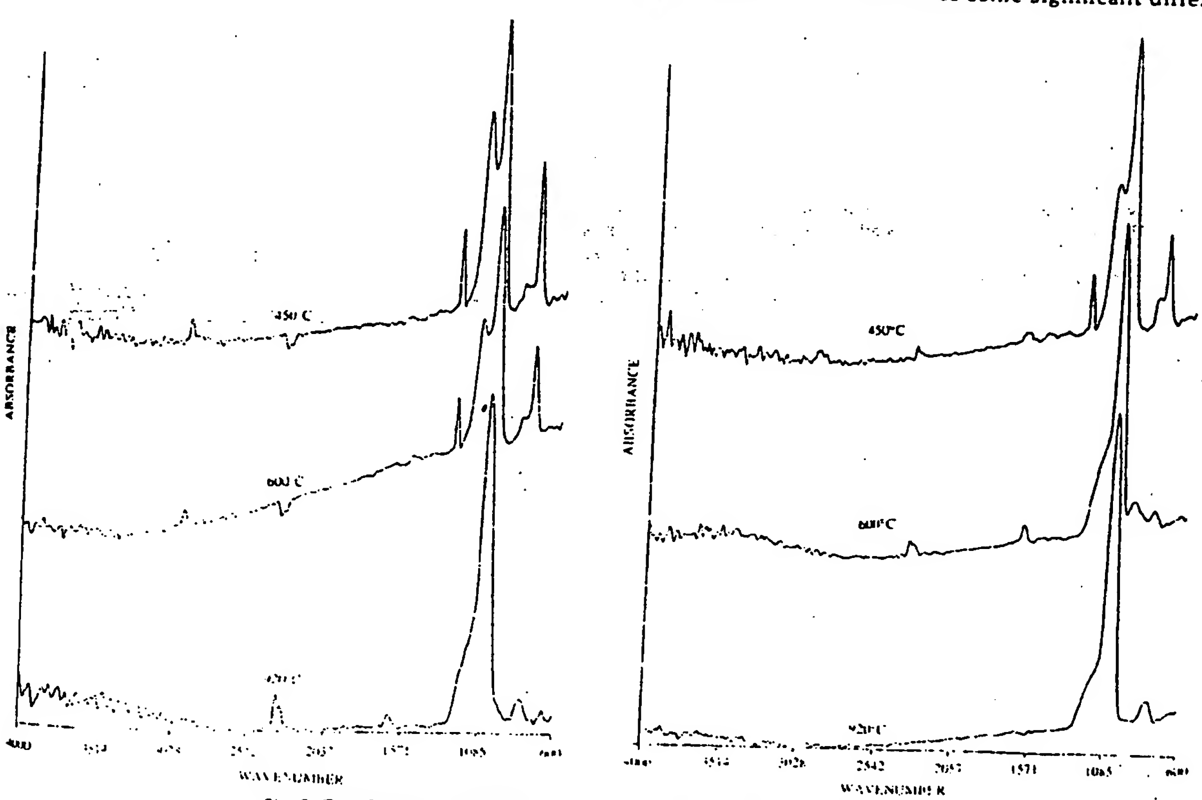

Fig. 5. The IR spectra of SOG-B after annealing in (a, left) N_2 and (b, right) O_2.

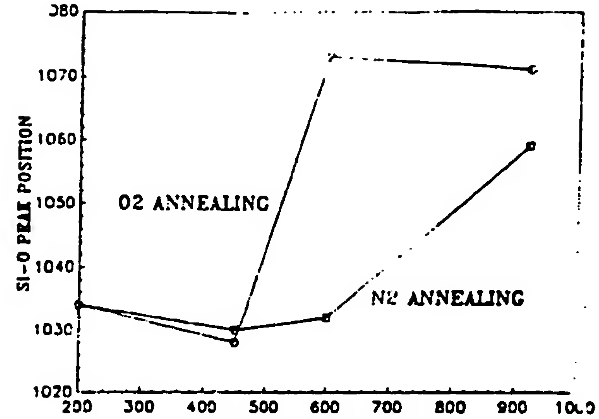

Fig. 6. Si—O peak positions vs. annealing temperatures for SOG-B

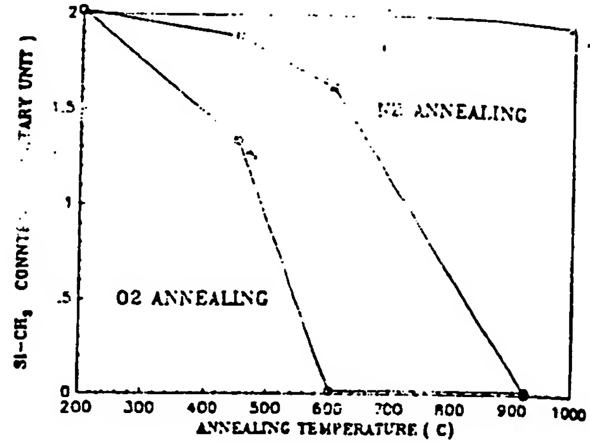

Fig. 8. Integrated Si—CH_3 peak areas for SOG-B vs. annealing temperatures.

ences between these two SOG materials. In Fig. 6, the initial peak position after the 200°C cure is much lower, and the drop upon heating to the 450°C is also much smaller than that observed for SOG-A. This is probably because all solvent for SOG-B, unlike SOG-A, has been removed by the 200°C bake. Other factors, such as lower initial Si—OH contents, may also be playing a role. For SOG-B, the oxygen ambient becomes effective at extracting organics and forming Si—OH at temperature above 450°C. This causes the observed shift to higher wave numbers. A similar effect of the nitrogen ambient does not begin until temperature greater than 600°C, and glass formation may not be complete, even at 920°C. Generally, SOG-A and B differ markedly in their solvent/polymer interaction.

As can be seen from Fig. 7, the OH content is very low after 450°C annealing in either O_2 or N_2 ambient. At 600°C, only O_2 annealing increases the OH concentration. Annealing at 920°C in O_2 can remove most of the OH groups from the film. The OH content from N_2 ambient remains low for all annealing temperatures. The organics (Fig. 8) are all gone in O_2 ambient at an annealing temperature of 600°C or higher. However the N_2 ambient cannot oxidize all of the CH_3 groups until 920°C. This is consistent with the interpretation given for Fig. 6.

The IR spectra of SOG-B are more sensitive to the annealing ambients for the temperature range studied than those of SOG-A: O_2 seems more effective in converting the SOG-B film into SiO_2 than N_2. Since aluminum metallization limits the processing temperature to 500°C or lower, SOG-B can provide a stable film with very little OH concentration with a 450°C annealing in O_2. This is important since the polar OH groups will respond to ac signals and thus increase the dielectric constants. If high temperatures are allowed, such as 920°C, both films possess good material properties.

Stress measurement.—The tensile stress from the volume shrinkage is the main reason why most of the SOG films crack. Two stress measurement systems were used to study the mechanical behavior of spin-on glass films: a room-temperature optically levered stress gauge (OLSG) for observing the films after annealing, and a hot stage stress gauge (HSSG) that permits *in situ* measuring of stress during annealing. In both systems, the radius of curvature of a wafer is measured by an optical lever and the bare wafers are measured prior to film deposition to eliminate the contribution of inherent wafer warpage. For the OLSG room-temperature system, a laser beam is reflected from the wafer as the wafer is translating across the beam spot and detected by a pin diode mounted on the translating stage. The radius is calculated from the displacement of the reflected beam. The same process is repeated at several points on the wafer to improve accuracy. The *in situ* HSSG system uses an oscillating mirror to scan a laser beam over the wafer surface instead of moving the wafer on a track as in the room temperature stress measurement system. The wafer is held stationary on a hot plate in the HSSG stress measurement system, and is separated from the cool ambient by a ceramic lid, which has a narrow slit that allows the laser to scan across the wafer (15). This system has a sensitivity for measuring the radius of curvature up to 3 km.

For a Si wafer with a small amount of wafer warpage, the stress in the film is given by (16)

$$\sigma_f = \frac{E_s}{6(1-\nu_s)} \frac{t_s^2}{R t_f}$$

where t_f is the film thickness, R is the radius of curvature, t_s is the Si substrate thickness, E_s is the Young's modulus

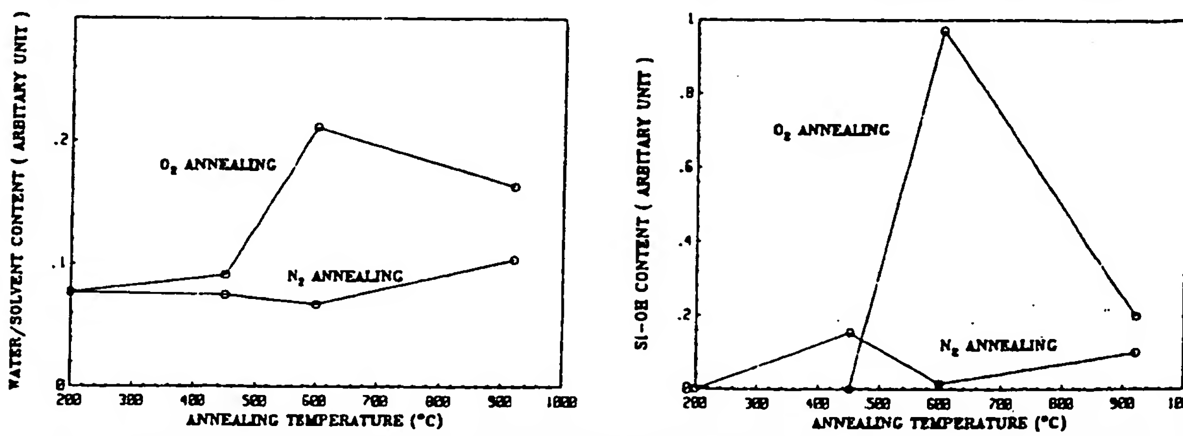

Fig. 7. Integrated IR peak areas for SOG-B vs. annealing temperatures for (a, left) the extended OH peak (3200-3800 cm^{-1}) and (b, right) Si—OH peak (940 cm^{-1}).

Table I. Dielectric constants of SOG's

Ambients	O_2						N_2			Steam
t_{anneal} (min)	30			1			30			60
T_{anneal} (°C)	450	600	920	450	600	900	450	600	920	50
SOG-A (10 kH)	(58)	(74)	(14)	N/A	N/A	N/A	(15)	(14)	(35)	(35)
SOG-A (1 MH)	(16)	(18)	9.6	N/A	N/A	N/A	(3.9)	(11)	(10)	13.5
SOG-B (10 kH)	4.2	(57)	9.0	6.4	(32)	9.0	3.4	2.8	8.9	5.4
SOG-B (1 MH)	2.3	(16)	7.7	(3.6)	(2.3)	(3.0)	(2.3)	(2.2)	(4.8)	3.0

constants of SOG-A, those of SOG-B are much less sensitive to the annealing ambients at 450°C. All annealing conditions give low dielectric constants and low dissipation factors except that annealed at 600°C in O_2 ambient. When annealed at 600°C, the film annealed in O_2 shows a much higher ϵ_r value and D value than in N_2. These data again have a strong correlation with the OH concentration in the film (low in N_2 and high in O_2 ambient). An interesting thing is that a 1 min annealing in O_2 (rapid thermal annealing) gives similar results to the 30 min annealing in a tube furnace, suggesting that the annealing process is not diffusion-limited. More extensive studies are needed to study the annealing time effect on the dielectric properties of SOG films.

Summary

The characteristics of two different types of SOG were studied as a function of their annealing temperatures and ambients. It has been established that different annealing conditions are required to optimize the dielectric properties for different SOG materials. The FTIR studies clearly showed the presence and absence of different organic groups after various annealing conditions. It can also be used to determine the presence of bonded OH groups and absorbed OH groups after various annealing conditions. The IR spectra studies show that the OH concentration in SOG-A films depends strongly on the annealing conditions. Inert ambient (N_2) generally introduces less OH content into the films than an oxidizing ambient (O_2) does. For SOG-A films, neither annealing at 450° nor at 600°C can drive off all the OH contents. Only after 920°C annealing can the film be dehydrated. However, SOG-B shows a very low OH content film after 450°C annealing for O_2, N_2 as well as steam ambient. The Si—O peak position and shifts observed can be interpreted in terms of the effects that solvent, organics, and silicon-bound OH have upon the Si—O bonding network. SOG-B after the initial 200°C bake has very little residual water/solvent, in contrast to SOG-A.

The residue stress after annealing as well as *in situ* stress during the annealing process have been determined for two different types of SOG materials. The stress levels of both SOG-A and SOG-B films are low tensile after 450° and 600°C annealings. The stress is relieved at 920°C and becomes compressive when cooled to room temperature.

The measured dielectric properties of the SOG films are also found to be sensitive to annealing conditions. Furthermore, a good correlation has been established between dielectric properties obtained from electrical measurements to that of OH concentration in the SOG films obtained from FTIR measurements. Dielectric constant and dissipation factor increase with OH concentrations. SOG-B films show good results after relatively low temperature annealings as required by the multilevel aluminum metallization processes. Both films provide good dielectric properties if high temperatures are allowed.

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REFERENCES

1. J. H. Kotani, H. Yakushiji, H. Harada, K. Tsukamoto, and T. Nishioka, *This Journal*, 130, 645 (1983).
2. S. Mercier, H. M. Naguib, V. Q. Ho, and H. Nentwich, *ibid.*, 132, 1219 (1985).
3. M. Morimoto, T. Mogami, H. Okabayashi, and E. Nagasawa, 1983 Symp. on VLSI Tech., 100 (1983).
4. C. Y. Ting, V. J. Vivalde, and H. G. Shafer, *J. Vac. Sci. Technol.*, 15, 1105 (1978).
5. A. M. Wilson, *Thin Solid Films*, 83, 145 (1983).
6. P. DeGeyter, G. Brasseur, and F. Coopmans, IEEE, 1986 VLSI Multilevel Interconn. Conf., 319 (1986).
7. F. Dupuis, Y. Shacham-Diamand, and W. G. Oldham, IEEE, 1985 Symp. on VLSI Tech., 52 (1985).
8. C. Ting, I. Avigal, and B. C. Lu, Proc. of Kodak Microelectronic Seminar, 139 (1982).
9. M. Nakamura, R. Kanazawa, and K. Sakai, *This Journal*, 133, 1167 (1986).
10. P. Elkins, K. Reinhardt, and R. Tang, IEEE, 1986 VLSI Multilevel Interconn. Conf., 102 (1986).
11. G. E. Whitwell, *ibid.*, 292 (1986).
12. J. Multani, J. K. Chu, S. Mittal, and J. Orton, *ibid.*, 474 (1986).
13. S. K. Gupta and S. W. Kirtley, *ibid.*, 506 (1986).
14. C. Ting, R. Roat, and N. Cox, Abstract 352, p. 529, The Electrochemical Society Extended Abstracts, Vol. 86-2, San Diego, CA, Oct. 19-24, 1986.
15. E. J. McInerney and P. A. Flinn, *IEEE/IRPS Proc.*, 264 (1982).
16. A. K. Sinha, H. J. Levinstein, and T. E. Smith, *J. Appl. Phys.*, 49, 2423 (1978).

of Si substrate [with a value of 1.689×10^{11} N/m² for the (100) orientation]. ν_s is the Poisson's ratio of the substrate (with a value of 0.064). The stress is tensile (positive in sign) if the warpage is concave on the coated side and is compressive (negative in sign) if convex.

Typical results obtained from room-temperature stress measurements of 6000Å thick SOG-A films are shown in Fig. 9. The stress is low for all the samples annealed in different conditions (less than 10^8 Pa). The tensile stress increased after 450°C annealing as compared to the as-prepared film with 200°C bake. This is due to additional film shrinkage at higher annealing temperatures. After 920°C annealing, the loss of all organics and SiOH, the formation of a denser SiO_2 glass, and some thermal relaxation of stress combine to give a compressive film. The results of room-temperature stress measurements for SOG-B gave similar results and the stress level is slightly lower than that of SOG-A.

Figure 10 shows the *in situ* stress measurements of 4000Å thick SOG-B to two maximum temperatures: 440° and 600°C. The curves labeled H represent the heating cycle with a heating rate of 10°C/min. The C-labeled curves represent the cooling cycle. The cooling rate is 10°C/min down to the chuck temperature of 100°C, then at a much slower rate as the air cooling is less effective below this temperature. The samples were held for 30 min at the highest temperatures, 440°C in (a) and 600°C in (b) between the heating cycle and the cooling cycle. Holding the film at the high temperature increases the tensile stress. The increase is larger for higher temperatures. During the cooling, the stress does not change at all. It remains almost the same stress level as that at 440°C, and is slightly lower than that at 600°C. Again all the stress is relatively low (around 10^8 Pa) compared to other deposited oxide films of comparable thickness. For SOG-B, the increase in tensile stress at temperature >200°C is small indicating that additional shrinkage for SOG-B is small.

Dielectric constant.—As an interlayer dielectric film, spin-on glasses should have a low dielectric constant. However, the dielectric constant of spin-on glass is sensitive to the OH content in the film due to the polarizability of Si—OH bonds. The dielectric constant is measured by capacitors fabricated on coated wafers by

$$\epsilon_r = \frac{Ct}{\epsilon_o A}$$

where ϵ_r is the relative dielectric constant, ϵ_o is the permittivity of vacuum with a value of 8.854×10^{-12} F/m, C is the measured capacitance, t is the film thickness, and A is the capacitor area. Since p-type silicon wafers were used, the top metal electrodes were always biased by a negative voltage, which results in accumulation of the majority carriers in the substrate and thus minimizes the effect of depletion capacitance from the wafer. The Si

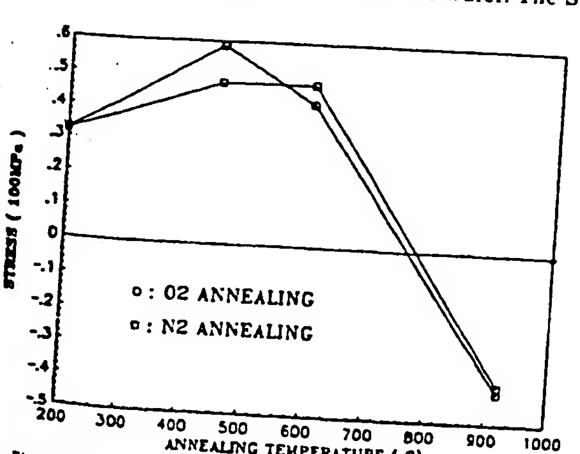

Fig. 9. Room temperature stress of SOG-A vs. annealing temperatures.

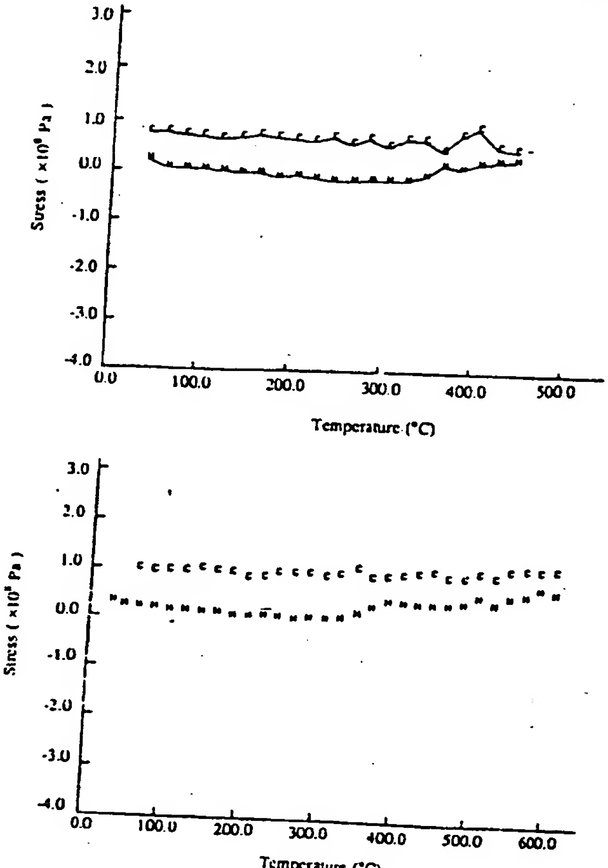

Fig. 10. *In situ stress measurements of SOG-B up to (a, top) 440°C and (b, bottom) 600°C.*

substrates were only moderately doped (resistivity about 15 Ω-cm), and thus the dissipation factor (D) increases at very high frequencies (generally over 4 MHz). Most of the data were corrected for D, but when the dissipation factor value is over 0.3, the measured dielectric constant is of doubtful value. These values are always in parentheses when presented.

Table I summarizes the dielectric measurement data for SOG-A and SOG-B. The data in parentheses are generally deviated from the true values by a small factor (less than 2). Therefore, it is safe to say that the annealing condition resulting in $\epsilon_r = 35$ does increase the dielectric constant by a large amount from that of a pure silicon dioxide film ($\epsilon_r = 3.9$).

In general, the dielectric constants of SOG-A are higher than those of SOG-B under the same annealing conditions. This is in agreement with the fact that the OH content in annealed SOG-A films are higher than that in SOG-B films as obtained from FTIR measurements. Another parameter associated with the OH content is the dissipation factor. High OH content tends to reduce the resistivity of the SOG film and increase D. SOG-A shows higher dissipation factors for most measurements, while the D values of SOG-B are low at 10 kHz for both the low temperature (450°C) annealed films and the high temperature (920°C) annealed films. The lowest dielectric constant of the 450°C annealed SOG-A films is in the N_2 ambient. The trends of ϵ_r of SOG-A in O_2 ambient (increasing from 450° to 600°C then decreasing to a much lower value at 920°C) and in N_2 ambient (decreasing slightly from 450° to 600°C) agree well with the trends of OH content changes for these annealing conditions. For 450°C annealing, SOG-A shows excessively high ϵ_r values and high D values. These undesirable dielectric properties make it difficult to implement SOG-A films into multilevel interconnection processes except when it is used in an etch-back process. Compared to the dielectric

Si substrate (with a value of 1.689 × 10^11 dyn/cm² for the (100) orientation), ν is the Poisson's ratio of the substrate (with a value of 0.064). The stress is tensile (positive in sign) if the warpage is concave on the coated side and is compressive (negative in sign) if convex.

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Dielectric constant.—As an interlayer dielectric film, spin-on glasses should have a low dielectric constant. However, the dielectric constant of spin-on glass is sensitive to the OH content in the film due to the polarizability of the OH bonds. The dielectric constant is measured by capacitors fabricated on coated wafers by

$$\epsilon_r = \frac{Ct}{\epsilon_o A}$$

where ϵ_r is the relative dielectric constant, ϵ_o is the permittivity of vacuum with a value of 8.854×10^{-12} F/m, C is the measured capacitance, t is the film thickness, and A is the capacitor area. Since p-type silicon wafers were used, the top metal electrodes were always biased by a negative voltage, which results in accumulation of the majority carriers in the substrate and thus minimizes the effect of depletion capacitance from the wafer. The Si

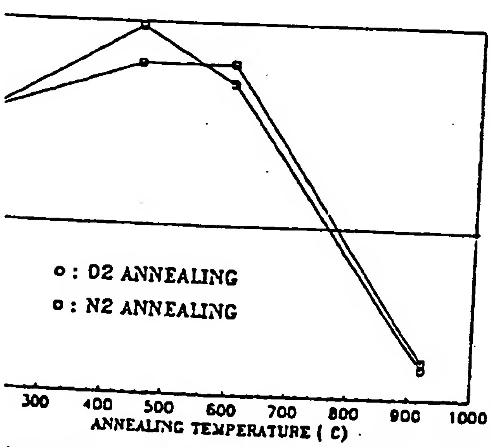

Fig. 9. Room temperature stress of SOG-A vs. annealing tempera-

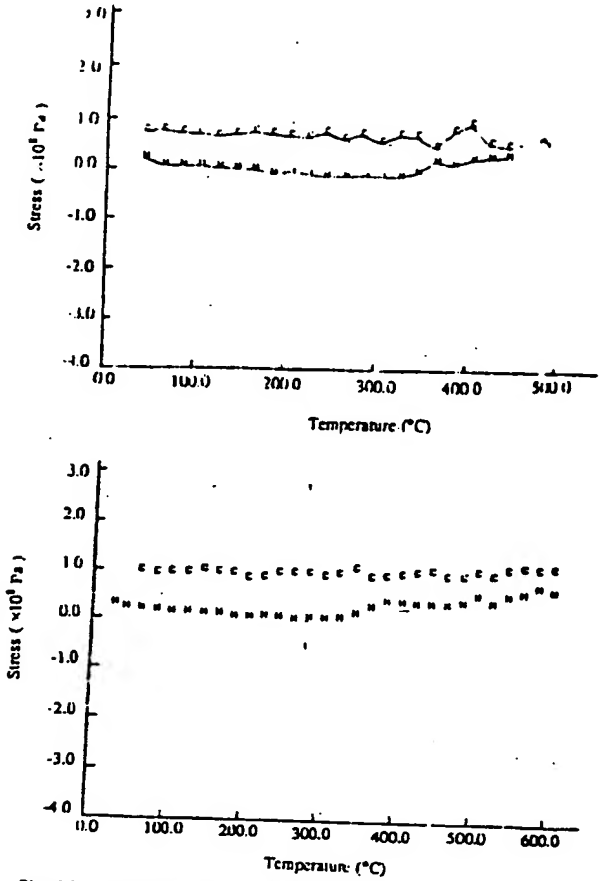

Fig. 10. *In situ* **stress measurements of SOG-B up to (a, top) 440°C and (b, bottom) 600°C.**

substrates were only moderately doped (resistivity about 15 Ω-cm), and thus the dissipation factor (D) increases at very high frequencies (generally over 4 MHz). Most of the data were corrected for D, but when the dissipation factor value is over 0.3, the measured dielectric constant is of doubtful value. These values are always in parentheses when presented.

Table I summarizes the dielectric measurement data for SOG-A and SOG-B. The data in parentheses are generally deviated from the true values by a small factor (less than 2). Therefore, it is safe to say that the annealing condition resulting in ϵ_r = 35 does increase the dielectric constant by a large amount from that of a pure silicon dioxide film (ϵ_r = 3.9).

In general, the dielectric constants of SOG-A are higher than those of SOG-B under the same annealing conditions. This is in agreement with the fact that the OH content in annealed SOG-A films are higher than that in SOG-B films as obtained from FTIR measurements. Another parameter associated with the OH content is the dissipation factor. High OH content tends to reduce the resistivity of the SOG film and increase D. SOG-A shows higher dissipation factors for most measurements, while the D values of SOG-B are low at 10 kHz for both the low temperature (450°C) annealed films and the high temperature (920°C) annealed films. The lowest dielectric constant of the 450°C annealed SOG-A films is in the N_2 ambient. The trends of ϵ_r of SOG-A in O_2 ambient (increasing from 450° to 600°C then decreasing to a much lower value at 920°C) and in N_2 ambient (decreasing slightly from 450° to 600°C) agree well with the trends of OH content changes for these annealing conditions. For 450°C annealing, SOG-A shows excessively high ϵ_r values and high D values. These undesirable dielectric properties make it difficult to implement SOG-A films into multilevel interconnection processes except when it is used in an etch-back process. Compared to the dielectric